PART I

ORGANIC BORON COMPOUNDS AS POLYMERIZATION CATALYSTS

By

ROBERT EDWARD ALLEN

A.B., Grinnell College, 1941

M.S., University of Illinois, 1942

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1944

URBANA, ILLINOIS

1944

PART I

ORGANIC BORON COMPOUNDS AS POLYMERIZATION CATALYSTS

By

ROBERT EDWARD ALLEN

A.B., Grinnell College, 1941

M.S., University of Illinois, 1942

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1944

URBANA, ILLINOIS

1944

ACKNOWLEDGMENT

The writer wishes to express his sincere appreciation to Dr. Harold R. Snyder for his many helpful suggestions and his encouraging interest during the course of this investigation.

INTRODUCTION

Boron fluoride has been used as a catalyst for polymerization of many vinyl monomers. Its behavior as a catalyst generally is believed to be due to the strong acceptor activity of the boron atom. The borines, represented by the general formula BR_3, might be expected to possess similar activity as electron-pair acceptors. The purpose of the present investigation was to determine whether the borines could be used as polymerization catalysts.

DISCUSSION

Trialkyl- and triarylborines have been prepared by the reactions of zinc dialkyls with ethyl borate,[1] or of Grignard reagents with boron fluoride.[2-3] The latter method was employed in synthesizing trimethyl-, tri-*n*-butyl- and tri-*t*-butylborines.

In testing the substances as catalysts, it was desirable to bring the borines into contact with the monomers under an atmosphere of nitrogen, since the trialkylborines are rapidly oxidized by air to produce alkaneboronic esters, $RB(OR)_2$.[3] This was accomplished by the use of a small nitrogen-filled hypodermic syringe which permitted both the measurement of the small amounts of borines and their injection into rubber-tipped reaction tubes containing the monomer under nitrogen.

Tri-*n*-butylborine caused vinyl acetate, vinyl chloride and methyl acrylate to polymerize rapidly, either in bulk or emulsion polymerizations. Styrene was polymerized at a much slower rate, and isobutylene and isoprene did not react under the influence of tri-*n*-butylborine. An attempt to isomerize methyl maleate by the catalytic action of this borine met with failure. No polymerization of linseed oil occurred when the borine was brought into contact with this drying oil.

Trimethylborine caused the rapid polymerization of vinyl acetate but styrene was not polymerized by this borine.

Tri-*t*-butylborine proved to be the most reactive of the three borines as a polymerization catalyst. It effected polymerization of vinyl acetate more rapidly than either trimethyl- or tri-*n*-butylborines. Vinyl acetate could be polymerized even in the presence of triethylamine, ethanol or hydroquinone. The amine would be expected to prevent the borine from reacting as a catalyst by converting it to the coordination compound. Hydroquinone generally is effective as an inhibitor in polymerizations brought about by peroxide catalysts.

The evidence does not permit a definite conclusion regarding the

mechanism of polymerization under the influence of borines. The fact that polymerization occurs in the presence of water, alcohol or triethylamine indicates that the polymerization is not ionic. It is more likely that traces of oxygen or peroxides present in the monomers convert some of the borine to peroxide, and this is the active catalyst.

BIBLIOGRAPHY

[1] Frankland, Ann., *115*, 319 (1860).
[2] Krause and Nitsche, Ber., *54*, 2784 (1921).
[3] Johnson, Snyder and Van Campen, J. Am. Chem. Soc., *60*, 115 (1938).

VITA

The author was born in Hampton, Iowa, December 27, 1919. He was graduated from the Hampton high school in 1937. He attended Grinnell College, Grinnell, Iowa, where he was granted the degree of Bachelor of Arts in June, 1941. In the fall of that year he began work in the Graduate School of the University of Illinois, where he received the degree of Master of Science in September, 1942. From September, 1941 to February, 1943 he held a teaching assistantship, and from February, 1943 to June, 1944 he held a special research assistantship.